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Atomic force microscopy in polymeric chemistry's studies

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Atomic force microscopy (AFM) is a unique method for polymeric surfaces visualization not only because of high lateral and vertical resolutions, but also its ability of gaining quantitative three-dimensional information about surface topography and roughness without destruction of a soft surface. Nowadays this method is oftentimes used to obtain only surface images, but polymeric surfaces contain much the largest information. Therefore it is relevant to open up AFM opportunities.

This work was aimed to develop a new approach based on AFM that allowed to establish a surface structuring mechanism of polymers during their modification (on the example of chitosan-based copolymers with polyacrylonitrile (PAN) and polystyrene (PS) modified with ionic liquids (ILs) with various anions) [1], to find out a dependence of polymers wettable, mechanical, and other functional properties on their surface structure (in particular on their roughness) (on the example polymeric films based on polysulfone (PSU), cellulose triacetate (CTA) and polyvinyl alcohol (PVA) obtained on glass substrates with different roughness), and to estimate a phase distribution at surfaces of polymer-based materials (on the example of the chitosan copolymers).

In the part of experiments with the chitosan copolymers, surface structuring features of chitosan (CS) graft and block copolymers with PAN and PS modified with ILs based on a cation of 1-butyl-3-methylimidazolium (bmim) with various anions ([BF_4], [PF_6] and [Tf_2N]) at each stage of modification were studied by step-by-step AFM scanning, and stability study of surface structure of the CS copolymers was estimated by mathematical statistics methods.

In the part of experiments with PSU, CTA, and PVA, an approach based on AFM combined with wettability measurements and mechanical testing was used. PSU, CTA and PVA polymer films were obtained by corresponding polymer solution casting using automatic coating machine MemcastPlus (Porometr, Belgium) onto three inert supports from borosilicate glass. The glass supports surface and the polymers surface were studied by a scanning probe microscope SPM-9700 (Shimadzu, Japan) using contact and tapping modes respectively. According to comparative analysis of the obtained AFM, mechanical testing, and wettability measurements results, it was found that (1) the higher intermolecular rotation freedom of a polymer, the more its surface reflects a support structure and its roughness (at significant values of supports roughness, this effect is brought to nothing); (2) polymers wetting decreases with an increase in their surface roughness because surfaces with significant roughness tend to be superhydrophobic and not wetted by most liquids; and (3) the nature of changes in polymer mechanical properties depends on their chain flexibility.

All this extensive information obtained by the proposed AFM-based approaches can be used to control polymers' functional properties by varying their surface roughness with regard to their chemical nature. This is important to develop a technique for formation of "smart" materials with given characteristics.

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1. T.S. Sazanova, K.V. Otvagina, I.V. Vorotyntsev, *Polymer Testing* **68**, 360 (2018).